Glass and Ceramics, Vol. 69, Nos. 7 – 8, November, 2012 (Russian Original, Nos. 7 – 8, July – August, 2012)

BIOMATERIALS

UDC 666.3:546.41'33'18

MULTIPHASE CERAMICS BASED ON POWDERS SYNTHESIZED FROM SODIUM PYROPHOSPHATE AND SOLUBLE CALCIUM SALTS USING MECHANICAL ACTIVATION

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Translated from *Steklo i Keramika*, No. 8, pp. 34 – 41, August, 2012.

A multiphase ceramics has been obtained from calcium phosphate powders synthesized by mechanical activation from sodium pyrophosphate and soluble calcium salts (acetate, nitrate, chloride). After synthesis from sodium pyrophosphate and calcium acetate or calcium nitrate the powders comprised a mixture of double calcium-sodium phosphate, unreacted calcium salt and reaction byproduct ($NaNO_3$ or $NaCH_3COO$). After synthesis from sodium pyrophosphate and calcium chloride the powders comprised a mixture of amorphous calcium phosphate and byproduct NaCl. After heat-treatment the phase composition of the samples depended on the firing temperature and the composition of the initial powders. After firing $Ca_2P_2O_7$, $Na_2CaP_2O_7$, $NaCaPO_4$ and $Ca_3(PO_4)_2$ were present in the samples.

Key words: mechanical activation, calcium pyrophosphate, double sodium calcium pyrophosphate — canaphite $CaNa_2P_2O_7 \cdot 4H_2O$, double sodium calcium orthophosphate — renanite $NaCaPO_4$, sodium pyrophosphate, porous ceramics.

Ceramic materials based on hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) and β-tricalcium phosphate ($Ca_3(PO_4)_2$, β-TCP) are widely used to eliminate bone-tissue defects. The compositional (bi-phase) ceramics Hap/β-TCP remains a subject of intense study and is used in medical practice as an osteoplastic material, since the resorption properties of this material can be varied by changing the ratio of the resorbed phase β-TCP and the HAp phase which is resorption stable (resistive). Phosphate glasses, calcium pyro- and polyphosphates [1] as well as double calcium/alkali-metal phosphates [2 – 4] are being studied as alternative resorbable phases. Calcium phosphate powders can be obtained by precipitation from solutions, by solid-phase reactions or from mixtures using mechano-chemical activation. The latter method requires prolonged milling of the initial powdered components in a solvent (usually, water) or in the absence of solvent (so-called dry mechano-synthesis) [5 – 7]. The following can occur in the process of synthesis using mechanical activation in powder mixtures containing a certain amount of solvent: a) exchange chemical reactions in saturated salt solutions usual for the dissolution method (since the solvent volume is limited) and b) decomposition and synthesis reactions as a result of the activation of reagent particles due to collisions between the particles themselves and with the milling bodies.

The objective of the present work was to obtain ceramics based on powders synthesized from sodium pyrophosphate and dissolved sodium salts using mechanical activation as well as to study the properties of synthesized powders and the phase composition of ceramics based on them.

EXPERIMENTAL PART

Mechanical activation of salt mixtures with the addition of a fixed amount of water was conducted in a Fritsch Analysette 5 (Model 05.32) planetary mill with milling drums (drum material — ZrO_2, volume 80 ml, radius 3.5 cm) using ZrO_2 milling bodies (diameter 0.8 cm, mass 1 g). Sodium pyrophosphate $Na_4P_2O_7 \cdot 10H_2O$ and calcium salt $CaX_2 \cdot nH_2O$ (Table 1), taken in amounts calculated to obtain 20 g mixture with Ca/P = 1 (theoretical), was placed in drums (mixture ratio salts : milling body = 1 : 3 by weight). Fifteen milliliters of salts were added to the mixture. The

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TABLE 1. Some Properties of Powders after Synthesis from Different Powdered Mixtures of Salts

Mixture	Salts used for synthesis		Post-milling phase composition	Post-synthesis rheological properties of powders	
				Bulk density, g/cm^3	Compact density, g/cm^3
1	$Na_4P_2O_7 \cdot 10H_2O$	$Ca(NO_3)_2 \cdot 4H_2O$	$CaNa_2P_2O_7 \cdot 4H_2O$ $NaNO_3$ $Ca(NO_3)_2 \cdot 4H_2O$	0.28	1.10
2	$Na_4P_2O_7 \cdot 10H_2O$	$CaCl_2$	$Ca_2P_2O_7 \cdot nH_2O$ (amorphous) NaCl	0.32	1.32
3	$Na_4P_2O_7 \cdot 10H_2O$	$Ca(CH_3COO)_2 \cdot H_2O$	$CaNa_2P_2O_7 \cdot 4H_2O$ $NaCH_3COO$ $Ca(CH_3COO)_2 \cdot H_2O$	0.35	1.41

suspensions were subjected to mechanical activation for 1 h with constant rotational speed of the wheel 600 rpm. Next, the product obtained was washed with fourfold distilled water on a paper filter (V_{water} = 200 ml) and dried in a thin layer at room temperature for 1 day. The powders obtained were disaggregated in acetone in the same mill (milling bodies : powder : acetone = 5 : 1 : 1 by weight, disaggregation time 5 min). After disaggregation and evaporatio of the acetone the powders were passed through a 200-μm sieve. Samples with dimensions 1.5 × 5 × 10 mm were pressed under pressure 100 MPa. To study the change of the phase composition of the powdered material the samples were fired at temperatures in the range 500 – 1000°C in steps 100°C and soaked at the final temperature for 6 h with heating rate 5 K/min.

X-ray diffraction studies were performed with a Rigaku D/Max-2500 diffractometer with a rotary anode (Japan). The measurements were performed in the reflection regime using CuK_α radiation (angular interval $2\theta = 2 – 60°$, step 0.02°, spectrum acquisition rate 5 K/min). The thermal analysis (TA) was performed in a NETZSCH 1200 thermal analyzer. The heating rate was 10 K/min and the temperature interval 30 – 1150°. The sample mass was at least 10 mg. The particle-size distribution was determined by static light scattering using a Fritsch Analysette 22 MicroTec Plus (Germany) laser diffraction analyzer. The sample microstructure was studied in a LEO SUPRA 50VP (Carl Zeiss, Germany) scanning electron microscope. The measurements were performed in a low-vacuum regime with accelerating voltage 20 kV. The ionic equilibrium in solutions containing pyrophosphate ions was modeled using the MEDUSA/HY-DRA software, including a data base on the equilibrium constants log K for acids, bases and complexes at 25°C [8]. The program use the SOLGASWATER [9] and HALTAFALL [10] algorithms.

RESULTS AND DISCUSSION

The solubility of the initial salts used for synthesis and reaction byproducts (RBP) — the corresponding sodium salts is presented in Table 2 [11]. Stoichiometric calculations show that the amount of water taken for synthesis (15 g + crystallization water of crystal hydrates) can completely dissolve the calcium chloride and nitrate (and a substantial portion of calcium acetate) present in the initial mixtures. However, sodium phosphate is the least soluble of the initial salts and not more than 30% dissolves even taking account of the possible local increase of the temperature to 60°C with mechanical activation. Analysis of the solubility of the sodium salts ($NaNO_3$, NaCl, $NaCH_3COO$) regarded as RBP shows that sodium chloride is least soluble. It can be concluded that the interaction during mechanical activation occurs in saturated solutions containing calcium and sodium cations, pyrophosphate anions and nondissolved sodium pyrophosphate. The acidity of the medium during the synthesis process is determined by hydrolysis of the pyrophosphate anion and an anion contained in the initial calcium salt and RBP.

Thus, three factors must be singled out. These could determine the composition of the products of synthesis during mechanical activation and serve as criteria for comparing the initial mixtures.

TABLE 2. Solubility of the Initial Salts and RBO [9] and Molar Ratio Ca/P Calculated for the Experimental High-Concentration Solutions

Salt	Solubility of matter in 100 g water		Ca/P in high-concentration solution during mechanical activation	
	20°C	60°C	20°C	60°C
	Initial salts			
$CaCl_2$	74.5	136.8	18.7	5.3
$Ca(NO_3)_2 \cdot 4H_2O$	129.3	281.5	8.4	2.4
$Ca(CH_3COO)_2 \cdot H_2O$	34.7	32.7	9.4	2.4
$Na_4P_2O_7 \cdot 10H_2O$	6.2	21.8	–	–
	Reaction Byproducts (RBP)			
NaCl	36.0	37.3	–	–
$NaNO_3$	88.0	124.0	–	–
$NaCH_3COO$	46.5	139.5	–	–

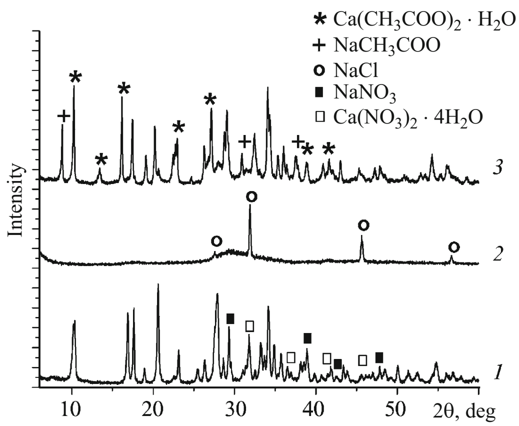

Fig. 1. XPA data for powders synthesized from the following salt mixtures: *1*) $Na_4P_2O_7 + Ca(NO_3)_2$; *2*) $Na_4P_2O_7 + CaCl_2$; *3*) $Na_4P_2O_7 + Ca(CH_3COO)_2$. The unmarked peaks belong to $CaNa_2P_2O_7 \cdot 4H_2O$.

The first factor is the concentration of calcium ions [Ca^{2+}]. From this standpoint the initial mixtures can be divided into two groups: the first one includes mixtures containing calcium nitrate and chloride, which are completely dissolvable in the amount of water taken for synthesis; the second group is represented by a mixture containing calcium acetate whose solubility is appreciably lower than that of the chloride and nitrate.

The second factor is the concentration of the sodium ion [Na^+]. From this standpoint the mixture initially containing calcium chloride and sodium chloride as the RBP, the least soluble salt among other sodium salts, differs from the other two mixtures by the fact that at the completion of synthesis the sodium cation concentration will be least in the high-concentration solution.

The third factor is the pH during synthesis. The initial alkaline pH is due to the hydrolysis of the pyrophosphate anion ($P_2O_7^{4-} + H_2O \leftrightarrow HP_2O_7^{3-} + OH^-$; $K_b = 10^{-14}/4.8 \times 10^{-10} = 2.1 \times 10^{-5}$ [11]). Subsequently, the pyrophosphate ion is bound in insoluble calcium pyrophosphate (or calcium/sodium). For this reason, the high pH can be retained as a result of hydrolysis of the anion entering into the composition of the calcium salt and RBP. In this sense, only in the mixture containing calcium acetate ($CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$; $K_b = 10^{-14}/1.7 \times 10^{-5} = 5.9 \times 10^{-10}$ [11]) can the alkaline reaction be maintained during the entire synthesis.

Since the regularities of the precipitation of pyrophosphates from high-concentration solutions have not been studied, it is desirable to analyze the equilibria existing in dilute solutions. The calculations show that in dilute solutions (concentration [$Ca^{2+} = 10$ mM]) calcium pyrophosphate (CPP) precipitates in the range pH = 4 – 9; increasing pH and decreasing Ca/P in solution make it soluble as a result of the accumulation of the ion complexes $CaP_2O_7^{2-}$ and $CaOHP_2O_7^{3-}$. Increasing the solution concentration expands the range of existence of CPP with respect to pH and Ca/P in the coordinates log [$P_2O_7^{4-}$] – pH. Initially, amorphous CPP precipitates from the solution; on contact with the mother liquor it crystallizes in time into CPP di- or tetrahydrate. According to the data obtained by the authors of the article, at room temperature this requires at least 2 days [12].

In summary, the reaction (1) reflects the expected course of the interaction in the experimental powdered mixture of the initial salts (see Table 1) with the use of mechanical activation. The degree of hydration and crystallinity of the precipitate of hydrated CPP can depend on the milling intensity and time:

$$Na_4P_2O_7 + 2Cax_2 + yH_2O \rightarrow Ca_2P_2O_7 \cdot yH_2O\downarrow + 4Nax, \quad (1)$$

where

$$x = NO_3^-, Cl^-, CH_3COO^-.$$

Nonetheless, according to XPA (Fig. 1, Table 1), after synthesis using mechanical activation double sodium/calcium pyrophosphate and RBP and calcium salt, which did not enter into reaction, were found in the compositions *1* (sodium pyrophosphate and calcium nitrate) and *3* (sodium pyrophosphate and calcium acetate). Sodium chloride and presumably amorphous CP were always found in the composition *2*. The XPA data for the composition *2* do not give any reason to assert that amorphous CP is the only product of the interaction of calcium chloride and sodium pyrophosphate, to rule out the formation of other phosphates or to confirm that the reaction (1) goes to completion. This result for the experimental mixtures can be attributed to the following chemical reactions:

$$Na_4P_2O_7 + Ca(NO_3)_2 + 4H_2O \rightarrow CaNa_2P_2O_7 \cdot 4H_2O\downarrow + 2NaNO_3; \quad (2)$$

$$Na_4P_2O_7 + 2CaCl_2 + yH_2O \rightarrow Ca_2P_2O_7 \cdot yH_2O\ (\text{amorphous})\downarrow + 4NaCl; \quad (3)$$

$$Na_4P_2O_7 + Ca(CH_3COO)_2 + 4H_2O \rightarrow CaNa_2P_2O_7 \cdot 4H_2O\downarrow + 2NaCH_3COO. \quad (4)$$

Formation of double calcium/sodium phosphate in mixtures *1* and *3* indicates to the importance of the factor attributed to [Na^+] concentration in the solution (see above). Presence of such a product in alkali solutions with high concentration of sodium cations can be explained through the following ionic reactions:

$$2Na^+ + CaP_2O_7^{2-} + 4H_2O \rightarrow CaNa_2P_2O_7 \cdot 4H_2O\downarrow, \quad (5)$$

$$2Na^+ + CaOHP_2O_7^{3-} + 4H_2O \rightarrow CaNa_2P_2O_7 \cdot 4H_2O\downarrow + OH^-. \quad (6)$$

The formation of hydrated double calcium/sodium pyrophosphate $CaNa_2P_2O_7 \cdot 4H_2O$ (canaphite) is quite unexpected for solution synthesis. Evidently, this compound

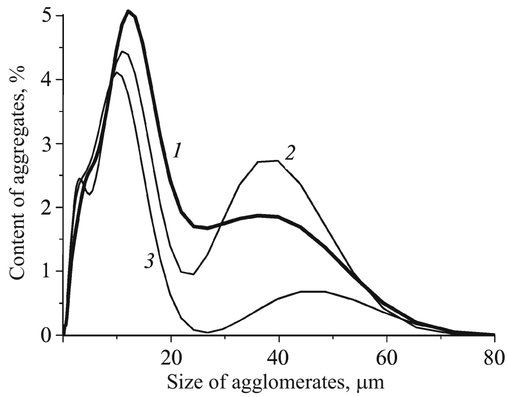

Fig. 2. Data from granulometric analysis for powders synthesized from the following salt mixtures: *1*) $Na_4P_2O_7 + Ca(NO_3)_2$; *2*) $Na_4P_2O_7 + CaCl_2$; *3*) $Na_4P_2O_7 + Ca(CH_3COO)_2$.

forms because high-concentration solutions with a high content of sodium cations form. In the literature, the formation of such compounds in an aqueous medium is mentioned in a description of the crystallization of pyrophosphates in solutions and gels with relatively high content of sodium salts as well as in [15] where hydrothermal synthesis was used [13, 14].

Thus, in accordance with XPA data and the proposed reactions $CaNa_2P_2O_7 \cdot 4H_2O$ (target product — CP), $NaNO_3$ (RBP), $Ca(NO_3)_2 \cdot 4H_2O$ (nonreacted initial component) are present in batch *1*; $Ca_2P_2O_7 \cdot H_2O$ (target product — amorphous CP; the possibility of partial substitution of Na for Ca in amorphous pyrophosphate cannot be ruled out), NaCl (RBP) and $CaCl_2$ (supposedly, as nonreacted initial component) cannot be ruled out; $CaNa_2P_2O_74H_2O$ (target product — CP), $NaCH_3COO$ (RBP), $Ca(CH_3COO)_2 \cdot H_2O$ (nonreacted initial component) in batch *3* (Table 3).

When synthesis is conducted using this method the byproducts of the reaction and the nonreacted initial salts remain in the powder after synthesis. The protocol used to remove the RBP (washing with a prescribed volume of distilled water) does not remove all ancillary components of the mixture (RBP of nonreacted salts).

According to the data from granulometric analysis (Fig. 2), the average size of agglomerates for all synthesized powders lies in the range 5 – 20 μm. The most likely size is 10 – 12 μm. Large aggregates 40 – 60 μm probably formed as a result of the binding action of the reaction byproducts (RBP).

Photomicrographs of the synthesized powders are presented in Fig. 3. The compositions *1* and *3* contained relatively large (to 1 μm) plate-shaped crystals and aggregates of the main phase $CaNa_2P_2O_7 \cdot 4H_2O$. The composition *2* includes smaller (<0.5 μm), isometric particles. The bulk density of the experimental powders ranged from 0.28 to 0.35 g/cm^3; the density of the compacts of the experimental powders ranged from 1.1 to 1.4 g/cm^3.

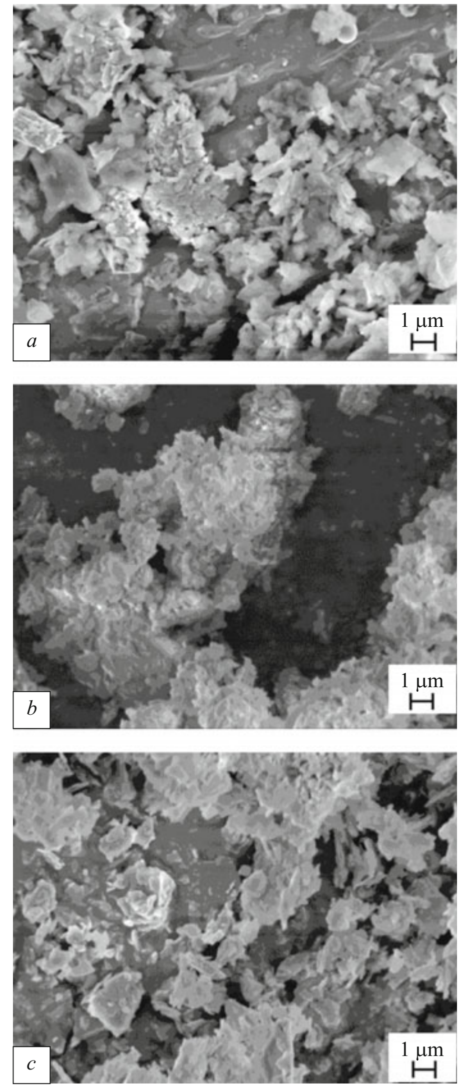

Fig. 3. Photomicrographs of powders synthesized from the following salt mixtures: *a*) composition (*1*) $Na_4P_2O_7 + Ca(NO_3)_2$; *b*) composition (*2*) $Na_4P_2O_7 + CaCl_2$; *c*) composition (*3*) $Na_4P_2O_7 + Ca(CH_3COO)_2$.

According to the thermal analysis data (Fig. 4), the mass loss was 25% for mixtures *1* and *3* and 2 – 20% for mixture *2*. The mass loss at temperature to 100°C is related with the removal of adsorbed water and acetone, since the disaggregation of the powders was done in acetone. The loss of water by crystal hydrates occurs at temperatures above 200°C. For all mixtures there is mass loss due to the presence of RBP or nonreacted salts. For samples *1* and *3* these are decomposition reactions of RBP and nonreacted salts. For sample *2* (RBP = NaCl) above the melting temperature of the chloride this is a liquid/gas phase transition. The mass loss at higher temperatures is due to RBP decomposition with release of gaseous substances and reactions leading to the formation of new substances.

According to XPA, in sample *1*, which was obtained using sodium pyrophosphate and calcium nitrate, crystalline

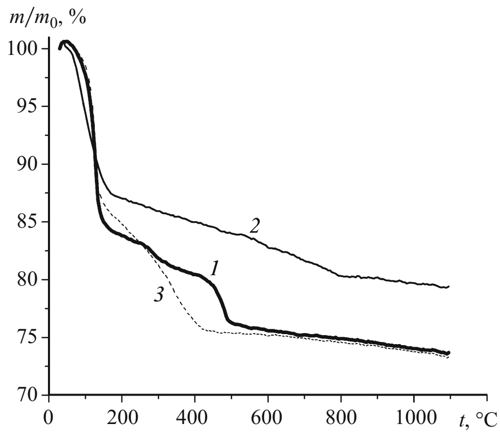

Fig. 4. Data from thermal analysis of powders synthesized from the following salt mixtures: *1*) $Na_4P_2O_7 + Ca(NO_3)_2$; *2*) $Na_4P_2O_7 + CaCl_2$; *3*) $Na_4P_2O_7 + Ca(CH_3COO)_2$.

calcium pyrophosphate $Ca_2P_7O_7$ (β-CPP) was observed after heat-treatment. β-CPP forms via the interaction of double calcium sodium pyrophosphate with calcium nitrate:

$$Na_2CaP_2O_7 + Ca(NO_3)_2 \rightarrow Ca_2P_2O_7 + 2NaNO_3. \quad (7)$$

The interaction of CPP with sodium nitrate (or the products of its decomposition) leads to the production of double sodium/calcium phosphate — renanite:

$$2Ca_2P_2O_7 + 4NaNO_3 \rightarrow 4NaCaPO_4 + 4NO_2 + O_2. \quad (8)$$

Renanite can also be formed via the interaction of double calcium/sodium phosphate with calcium phosphate (or the products of its thermal decomposition; the reaction with calcium oxide is presented):

$$Na_2CaP_2O_7 + CaO \rightarrow 2NaCaPO_4. \quad (9)$$

The formation of TCP at high temperatures is a result of the interaction of CPP with the products of decomposition of calcium nitrate, most likely with calcium oxide, which forms when calcium nitrate decomposes at temperatures above 600°C:

$$CaO + Ca_2P_2O_7 \rightarrow Ca_3(PO_4)_2. \quad (10)$$

According to XPA (Table 3), in sample *2*, which is obtained using sodium pyrophosphate and calcium chloride, CPP as well as renanite and chloro-apatite are observed after heat-treatment. On heating mixture *2* CPP is formed as a result of the thermal conversion of hydrated CPP via the reaction (11). Renanite can form as a result of the reaction (12). Chloro-apatite $Ca_5(PO_4)_3Cl$, for which Ca/P = 1.67 and differs substantially from Ca/P = 1 prescribed during synthesis, can form at least because of excess $CaCl_2$ in the powder system on firing. A small excess of $CaCl_2$ in the powder system can be formed because of the reaction (3), reflecting the interaction of calcium chloride and sodium pyrophosphate, does not go to completion possibly because of the lower solubility of sodium salts (sodium pyrophosphate and sodium chloride). In this case Ca/P in the concentrated solution will exceed the prescribed ratio Ca/P = 1. At high temperatures calcium chloride will interact with CPP via the reactions (13), (14):

$$Ca_2P_2O_7 \cdot xH_2O \rightarrow Ca_2P_2O_7 + xH_2O; \quad (11)$$

$$Ca_2P_2O_7 + 2NaCl + H_2O_{(vapor)} \rightarrow 2NaCaPO_4 + 2HCl\uparrow; \quad (12)$$

$$2Ca_2P_2O_7 + 2CaCl_2 + 2H_2O_{(vapor)} \rightarrow 2Ca_3(PO_4)_2 + 4HCl; \quad (13)$$

$$3Ca_3(PO_4)_2 + CaCl_2 \rightarrow 2Ca_5(PO_4)_3Cl. \quad (14)$$

A change of the molar ratio Ca/P in the powdered system to values >1 is also possible due to removal of phosphorus

TABLE 3. Phase Composition of Samples Before and After Heat-Treatment (Temperature 500 – 900°C), According to XPA Data

Mixture	Composition before heat-treatment	Composition after heat-treatment		
		500°C	700°C	900°C
1	$CaNa_2P_2O_7 \cdot 4H_2O$ $NaNO_3$ $Ca(NO_3)_2 \cdot 4H_2O$	$Na_2CaP_2O_7$ $Ca(NO_3)_2$ γ-$Ca_2P_2O_7$ β-$NaCaPO_4$	β-$Ca_2P_2O_7$ β-$NaCaPO_4$	β-$Ca_2P_2O_7$ β-$NaCaPO_4$ β-$Ca_3(PO_4)_2$
2	$Ca_2P_2O_7 \cdot nH_2O$ NaCl ...	γ-$Ca_2P_2O_7$ β-$NaCaPO_4$ $Ca_5(PO_4)_3Cl$	β-$Ca_2P_2O_7$ β-$NaCaPO_4$ $Ca_5(PO_4)_3Cl$	β-$Ca_2P_2O_7$ β-$NaCaPO_4$ $Ca_5(PO_4)_3Cl$
3	$CaNa_2P_2O_7 \cdot 4H_2O$ $NaCH_3COO$ $Ca(CH_3COO)_2 \cdot H_2O$	$Na_2CaP_2O_7$ γ-$Ca_2P_2O_7$ β-$NaCaPO_4$ $CaCO_3$ Na_2CO_3	β-$Ca_2P_2O_7$ β-$NaCaPO_4$	β-$Ca_2P_2O_7$ β-$NaCaPO_4$

from the system in the form of compounds containing PO_3^- in the form of either HPO_3 or $NaPO_3$ from melt formed at low temperatures. This supposition is supported by the endothermal peak in the interval 460 – 480°C on the DTA curve for sample *2* (curve not shown). The lowest temperature of the eutectic in the system $CaO–P_2O_5–Na_2O$ is T_{eut} = 536°C. However, aside from the indicated oxides NaCl is present in the system in adequate quantities. Undoubtedly, this will lower the formation temperature of a possible melt.

According to XPA, in sample *3*, which is obtained using sodium pyrophosphate and calcium acetate, CPP and renanite are present after heat-treatment. The formation of the phase composition of ceramic material can be described by the reactions

$$2NaCH_3COO \rightarrow Na_2CO_3 + (CH_3)_2CO; \quad (15)$$

$$Ca_2P_2O_7 + Na_2CO_3 \rightarrow 2NaCaPO_4 + CO_2\uparrow. \quad (16)$$

The method of isothermal soakings was used to investigate the lineal shrinkage and the change of the density of the samples. The temperature dependence of the shrinkage is linear. The maximum shrinkage reaches 25% in the interval 750 – 850°C. The density of the samples *1* and *2* reaches its maximum value 1.94 and 1.70 g/cm^3, respectively, at 800°C and 2.08 g/cm^3 at 700°C for sample *3*.

For samples *1* and *2*, after firing at 900°C the porosities are comparable and equal about 30% (Fig. 5). For sample *3*, the porosity is 80% (Fig. 5), and pore size 300 – 500 μm. Pore formation is due to the release of gaseous products during the decomposition of the components.

The particle size in all samples after firing at 500°C does not exceed 500 nm. The particle size in all samples after firing at 700°C lies in the interval 1 – 3 mm. Comparing the particle sizes in the initial and heat-treated powders shows that the release of substantial quantities of gaseous products (mainly water vapor) during thermolysis promotes decomposition of quite large primary crystals.

After firing at 900°C for samples obtained from powder *1* 3 – 5 μm grains and large 20 – 30 μm grains can be seen in the material. After firing at 900°C for samples obtained from powder *2* the presence of melt promotes growth of crystals in the form of elongated hexagonal prisms with length to transverse size ratio 10 : 1 and longitudinal size not exceeding 20 μm in the material. After firing at 900°C for samples obtained from the powder *3* the grain size (15 – 25 μm) is many-fold greater than the grain size obtain by firing at 500°C (50 – 100 nm). The growth of grains at high temperature is due to dissolution-crystallization processes in the presence of melt in the system $CaO–P_2O_5–Na_2O$. In all probability, melts have different compositions, which is why different microstructures form at 900°C: the microstructure consists of small and large grains in the first case, elongated crystals in the second case and uniform grain growth in the third case. At 700°C a quite uniform rough surface forms, and in the opinion of the authors could promote spreading and growth of bone cells — osteoblasts — when such materials are used as substrates for cell cultivation.

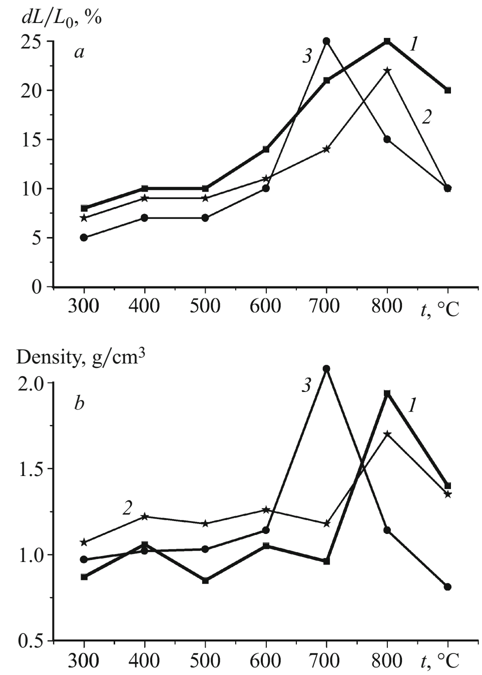

Fig. 5. Lineal shrinkage (*a*) and density (*b*) versus temperature in a study of samples of powders by isothermal soakings synthesized from the following salt mixtures: *1*) $Na_4P_2O_7 + Ca(NO_3)_2$; *2*) $Na_4P_2O_7 + CaCl_2$; *3*) $Na_4P_2O_7 + Ca(CH_3COO)_2$.

CONCLUSIONS

In the present work mechanical activation was used to perform synthesis from soluble salts in the presence of a small volume of solvent. Synthesis was performed using a suspension of initial salts in high-concentration solutions with effective mixing of the reagents by milling bodies. Complex heterogeneous processes can occur in such powered systems under mechanical activation. It should be noted that synthesis under such conditions occurs with high supersaturation relative to the low-solubility phosphate salt. High supersaturation promotes the formation of nanosize (or even amorphous) powders of the target phase. Evidently, such powders must exhibit high activity during sintering. The diversity of processes leading to the formation of powered products of synthesis with diverse phase compositions is largely determined by the solubility of the reaction byproducts. Resorbable calcium pyrophosphate and renanite form in the experimental mixtures at high temperatures. The ceramics obtained can be recommended for subsequent biomedical experiments on its possible use as bone transplant material, as a carrier of pharmaceutical preparations or as a porous resorbable component of structures for tissue engineering.

This work was performed as part of the Special Federal Program "Federal and Scientific-Pedagogical Cadres of Innovating Russia for 2009 – 2012" (measure 1.2.2, government contract No. 14.740.11.0277) and with the support of RFFI grants 10-03-00866, 12-03-01025, 12-08-00681 and 11-03-12179-ofi-m-2011. The equipment used in this work was acquired with support from the Program for the Development of Moscow University.

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